EP 118 625 A2

EP 0 118 625 A2

Translated from German by the Ralph McElroy Co., Custom Division
P. O. Box 4828, Austin, TX 78765 USA

Code: 1505-58979

EUROPEAN
~~FEDERAL REPUBLIC OF GERMANY~~
PATENT OFFICE
PATENT NO. 0 118 625 A2

Int. Cl.^{3}: A 61 L 9/04
A 61 L 9/01

Application No.: 83113258.4

Application Date: December 31, 1983

Publication Date: September 19, 1984
Bulletin 84/38

Priority:
Date: February 11, 1983
Country: DE
No.: 3304822
Date: March 30, 1983
Country: DE
No. 3311642

AN ODOR IMPROVER AND A METHOD FOR ITS MANUFACTURE

Applicant: Dr. O. Martens & Co.
Nachf.
Oberdillerstrasse 18
D-8021 Baierbrunn (DE)

Inventors: Dr. Bruno Storp
Rotwandstrasse 8
D-8023 Gosshesselohe
(DE)

Dr. Walter Steiner
Ludwig-Dürr-Strasse 9
D-8021 Icking (DE)

Representative: Horst-Rüdiger Kressin et al.
DIEHL & KRESSIN
Flüggenstrasse 17
D-8000 München 19 (DE)

The invention concerns an odor improver based on hexaalkylcyclotrisiloxane and a perfume and/or perfume mixture. The odor improver optionally additionally contains a compound that reduces the evaporation rate of the hexaalkylcyclotrisiloxane and additionally other cosmetic or disinfectant agents. The odor improvers in accordance with the invention can be used, as a room air freshener, in toilet beads and for adding fragrance to textiles.

An odor improver and a method for its manufacture

The invention concerns an odor improver based on a perfume vehicle and a perfume or perfume mixture.

The use of elastic, cold-moldable methylphenylpolysiloxane as embedding medium for perfume is known from DE-AS 10 63 309. The known polysiloxane media serve to extend the release of the perfume over a longer time. However, the known embedding media have the disadvantage that they do not evaporate, but rather remain after delivery of the perfume and thus the end of the release of perfume is not discernable or is only very poorly discernable.

The invention had the task of making available an odor improver that evaporates as much as possible at room temperature in order to make the end of the delivery of perfume discernable to the user. An additional task is to make available a physiologically harmless odor improver that does not give rise to any offensive order. Another task is to make available an odor improver that can be sprayed or that floats in water.

The task is solved by an odor improver that contains a hexalkylcyclotrisiloxane and optionally other evaporable or nonevaporable additives to reduce the sublimation rate of the hexaalkylcyclotrisiloxane and optionally other well-known auxiliary agents.

Especially suitable as perfume vehicle materials are hexamethyl-, hexaethyl-, hexapropyl-, hexaisopropyl-, hexabutyl- or hexa-t-butylcyclotrisiloxane.

The most suitable vehicle material is hexamethylcyclotrisiloxane, which has a melting point of about 64-66°C and evaporates relatively rapidly at room temperature.

The odor improver in accordance with the invention is used in particular as a room air freshener, toilet flush additive, for toilet beads, for floating odor improvers in toilet tanks, as a sprayable aerosol mixture, etc.

In each case according to purpose, a solid hexaalkylcyclotrisiloxane or a liquid hexaalkylcyclotrisiloxane is preferably used. For example, hexaethylcyclotrisiloxane* can be advantageously used for sprayable aerosol mixtures.

Suitable perfumes for the vehicle material in accordance with the invention are natural and synthetic perfumes,

---

* [Translator's note: sic; see below, especially Example 15]

especially ones that contain, for example, alcohol, ether, ester, aldehyde, keto, acid, nitrile, nitro groups as functional groups or a terpene or sesquiterpene group, for example anethol, anisaldehyde, vanillin or citronellal. N-containing organic compounds and aliphatic and aromatic hydrocarbons with saturated and/or unsaturated substituents can be used as suitable perfumes. Suitable essential oils are, for example, anise oil, bergamot oil, camphor oil, citronella oil, lemon oil, eucalyptus oil, pine needle oil, geranium oil, lavender oil, lemongrass oil, oil of clove, oil of orange, orange flower oil, peppermint oil, oil of roses, oil of spike lavender, oil of turpentine, and cinnamon oil.

The amount of the hexaalkylcyclotrisiloxane compound is 0.5-98% by weight, in particular 2-60% by weight, with respect to the total weight of the odor improver. The amount of perfume or perfume composition is 2-50% by weight, especially 3-12% by weight, with respect to the total weight of the odor improver.

The vehicle material used in accordance with the invention can contain stabilizers, which prevent or delay polymerization of the evaporable siloxane compound to nonevaporable, highly polymerized siloxane compounds. In this way, a possible adverse effect on the part of the evaporation rate of the vehicle materials in accordance with the invention, which can arise with lengthy storage, is largely prevented. Alkaline earth metal oxides, especially MgO, BaO, and/or CaO, for example, are suitable as stabilizers for hexaalkylcyclotrisiloxanes. The amount of the optionally used stabilizer is 0.1-1% by weight, with respect to the weight of the hexaalkylcyclotrisiloxane.

The sublimation rate of the hexaalkylcyclotrisiloxane, especially hexamethylcyclotrisiloxane, makes itself

advantageously felt if the siloxane is used as a lift for the perfume oil, i.e., when the odor improver consists only of the siloxane and perfume oil and the siloxane is used in a small amount, for example up to 0.5-30%, with respect to the total weight of perfume oil and siloxane.

The sublimation rate of the hexaalkylcyclotrisiloxane is too high for some applications. For this reason, additional agents that lower the sublimation rate of the siloxane are added to the vehicle material. The odor improver can also, however, be coated with added materials that solidify at room temperature after application and that reduce the sublimation rate. Suitable added agents are, for example, paraffin, stearin, paraffin oil, esters of resin acids, polyamide resins, ethylcellulose, vinyl acetate-vinyl chloride mixed polymerizates, polyvinyl alcohol, gelatin, starch, epoxy resins, polychloroprenes, polyisobutylene, camphor, naphthalene, tetramethylcyclobutanedione, trialkyltrioxane, adhesive substances, camphene, tricyclodecane, montan resin, montan wax, polyvinylacetate, polyvinylpyrrolidone, calcium carbonate, clay, soap, aluminum oxide, resinoids, water glass, silicates, silicas, coumarone-indene resins, acrylonitrile-butadiene mixed polymerizates, polyvinyl propionate, cellulose derivatives such as methylcellulose, melamine-formaldehyde resin, furan resins, polyurethanes, casein, alginates, glutin and/or dextrin.

The added agents are, provided solids are concerned, mixed into the perfume vehicle in a very finely divided form, with the particle size of the additives not being critical. However, they are preferably around 0.5 mm and smaller. Solid, nonevaporable additives are distributed as homogeneously as possible in the odor improver and are present only in a small amount, so that

they accumulate in a uniformly finely divided form as the perfume vehicle and the perfume evaporate.

The additive can also consist of a solid that imparts buoyancy to the odor improver in water, for example foam particles of polyurethane or polystyrene. These odor improvers are buoyant and for this reason are preferably used for toilet tanks. In addition, the odor improvers preferably contain additionally surfactants and/or disinfectants.

The added agents can be both mixed with the siloxane vehicle material and/or be applied as a coating to the odor improver.

Additives that are soluble in water and/or a solvent can be applied to the siloxane vehicle material in the form of a solution. This can be done, for example, by dipping the odor improver in a solution or by spraying the solution onto the surface of the odor improver. After application of the solution the solvent is removed by evaporation. The operation of dipping or spraying can also be carried out several times. However, sublimation of the siloxane vehicle material should not be completely prevented.

The added agent to the surface of the odor improver consisting of hexaalkylcyclotrisiloxane, perfume, and optionally additional agents, can also be applied by immersion into a melt of the added agent. The thickness of the coating of the melt of added agent can be adjusted, for example by several immersions into the melt, so that the desired sublimation rate of the siloxane vehicle material is attained. In this way, the desired sublimation rate can be adjusted to the relevant application by means of a simple laboratory test. The level of water-solubility of an odor improver containing a water-soluble substance can

also be affected in the desired way by the kind and thickness of the coating.

The added agents are in general in an amount of 6-50% by weight, especially 10-40% by weight, with respect to the total weight of the odor improver.

In accordance with one embodiment of the invention, the odor improver can also consist of a propellent gas, a hexaalkylcyclotrisiloxane, especially hexamethylcyclotrisiloxane, and a perfume oil. A fluorocarbon, propane or butane can, for example, be used as propellent gas. The perfume oil or perfume composition can also be replaced by a disinfectant, provided the disinfectant does not have an unpleasant order.

The aerosol mixture can optionally contain disinfectants in addition to the perfume oil. The aerosol mixture is charged to the spray devices under pressure. The aerosol mixture can be sprayed as a white dry powder that evaporates without leaving a residue, in particular in dependence on the amount that is sprayed. The aerosol mixtures are especially suitable as room air fresheners, clothing sprays, furniture sprays, as well as a Christmas spray to produce artificial snow. The advantage of the spray lies in the fact that the odor can be dispensed precisely with regard to the strength and time and the user immediately recognizes when the source of the odor is used up, namely by the fact that the sprayed material has evaporated. In the case of bathroom disinfectant sprays, the amount of added perfume oil can be relatively low or it can also be left out entirely. The amount of hexaalkylcyclotrisiloxane, especially hexamethylcyclotrisiloxane in the aerosol mixtures is around 20-

60% by weight, with respect to the total weight of the liquid aerosol mixture.

It can be advantageous that the perfume vehicle for special applications, for example, when it is used as a toilet bead, contain washing aids, surfactants and/or disinfectants. All of the substantially known surfactants can be used as surfactants, for example, anionic, cationic, nonionic and amphoteric surfactants such as soaps, sulfonates, amine salts, invert soaps, quaternary ammonium compounds, ethoxylates, amine oxides and/or betaines.

Urea, sodium sulfate and/or sodium carbonate may, for example, be considered as washing aids.

Coarsely divided disinfectants, which are suitable for combating pathogenic microorganisms, are especially used as disinfectants, for example, chlorates, hypochlorides, bleaching powder, chloramines, methyl and/or chlorine derivatives of phenol, quinoline, acridine, quaternary ammonium compounds, amphoteric surfactants and mixtures thereof.

The surfactants and washing aids serve for simultaneous cleaning of the toilet bowl in which the odor improvers in accordance with the invention are placed. The amount of the auxiliary agents (surfactants, washing aids and/or disinfectants) is 3-15% by weight, especially 5-10% by weight, either as individual compounds or as a mixture, with respect to the total weight of the odor improver.

The odor improvers in accordance with the invention can be made by homogeneously mixing the hexa(C_1-C_4-alkyl)-cyclotrisiloxane compound with the perfume component or the perfume composition and optionally adding the additives and then pressing the mixture into a perfume vehicle form under the

application of pressure and optionally under the additional effect of heat. Pressing of the constituents of the perfume vehicle can be done using the traditional presses that are suitable for making tablets or beads or capsules.

An especially homogeneous and dense packing form is produced when the constituents of the perfume vehicle material are mixed with each other in the melt and then cooled.

The reduction of the sublimation rate of the siloxane used in accordance with the invention, can according to an advantageous embodiment, also be attained by providing the solid perfume vehicle materials with a coating that reduces sublimation, especially one consisting of polyvinyl alcohol, polyvinyl pyrrolidone, montan wax, montan resin and/or tricyclodecane. The molded articles of hexaalkylcyclotrisiloxane, especially hexamethylcyclotrisiloxane, and perfume are preferably immersed in an immersion bath containing the sublimation-reducing additive as a melt or solution in order to apply the coating. An especially suitable immersion bath consists of, for example, a solution of polyvinylacetate and/or polypyrrolidone in an alkylalcohol, such as methanol, ethanol, isopropanol. Here, added agents that likewise sublime but have a lower sublimation rate than hexamethylcyclotrisiloxane are used especially as the coating materials. Especially camphor, camphene, tricyclodecane and/or tetramethylcyclobutanedion are suitable for this purpose.

In addition, it was established that a hexaalkylcyclotrisiloxane, especially hexamethylcyclotrisiloxane, acts as a lift for the perfume that is used. This becomes especially advantageous in the case of perfumes with low vapor pressure.

According to a particular embodiment of the invention, additives that have a fair amount of perfume effect, for example camphor, camphene, tricyclodecane, and quite a few disinfectants can also be used. In this case, one can do away with the use of a perfume oil if the application allows.

Especially preferred as additives for reducing the sublimation rate of hexamethylcyclotrisiloxane is a trialkyltrioxane. Especially preferred is a tri(C_3-C_6-alkyl)-trioxane, in particular triisopropyltrioxane and tri-t-butyltrioxane. The invention is illustrated more closely by the following examples:

Example 1

4.75 g hexamethylcyclotrisiloxane was mixed with 0.25 g terpineol and then pressed into a loosely packed tablet. When the tablet was left at room temperature 50% (2.5 g) of the perfumed body had evaporated after 5 days.

Example 2

20 g hexamethylcyclotrisiloxane was dissolved in 80 g of the perfume composition "drom C". The perfume composition "drom C" consists of

10 g citronellal
40 g citronella oil Java
9 g citronellol
1 g "aldehyde 16"
10 g benzyl acetate
20 g litcea cubeba oil

10 g terpineol

Incorporated in soap or when cellulose is soaked with the solution, this mixture produces a more intensive order than when the perfume composition is used without the siloxane. The siloxane thus acts as a "lift" for the perfume.

Example 3

3.5 g hexamethylcyclotrisiloxane, 2 g paraffin oil and 0.5 g terpineol oil were mixed with each other and then pressed into a spherical perfume vehicle (loosely packed powder). When the sample was left at room temperature 2 g (33.3%) of the perfumed body had evaporated after 25 days.

Example 4

2.5 g hexamethylcyclotrisiloxane, 2 g camphor and 0.05 g of perfume composition "drom C" was mixed and then pressed into a loosely packed tablet. The perfume composition "drom C" is identical to the composition described in Example 2.

The sample was stored at room temperature and then the sublimation rate was determined. After storage of 14 days, a total of 3 g of the perfumed body had evaporated.

Example 5

A sample was prepared from 3 g hexamethylcyclotrisiloxane, 0.6 g of perfume composition "drom C" and 2.4 g paraffin wax as sublimation-inhibiting additive. 2.8 g of the perfumed body had evaporated after about 15 days.

Example 6

A sample was prepared from 3 g hexamethylcyclotrisiloxane, 0.6 g perfume composition "drom C" and 2.4 g polyethylene glycol with a molecular weight of 1500-4000 as additive. About 2.5 g of the substances had evaporated after 14 days.

Example 7

5 g hexamethylcyclotrisiloxane, 3 g ethyl cellulose and 1 g terpineol oil were mixed and the powder prepared in this way was tested with regard to the sublimation rate. It was established that when stored at room temperature, 3.5 g of the powder had evaporated after 16 days.

Example 8

5 g hexamethylcyclotrisiloxane was mixed with 0.5 g terpineol oil and pressed into a tablet. The tablet thus prepared was coated with a polyurethane varnish. The coating can be made by spraying or by dipping into a polyurethane varnish bath. The evaporation rate of the siloxane was considerably reduced by the coating.

Example 9

3.5 g hexamethylcyclotrisiloxane was mixed with 2 g paraffin oil and 0.5 g terpineol oil and pressed to a flat lenticular tablet. Then, the thus prepared tablet was coated on both sides with a vapor-permeable synthetic film. When the thus prepared tablet was stored at room temperature, a considerable reduction of the sublimation rate compared to the uncoated tablet was found. Only 0.5 g of the perfumed body had evaporated after 25 days.

Example 10

6.2 g hexamethylcyclotrisiloxane was homogeneously mixed with 0.3 g silica gel, 0.5 g paraffin wax, 2 g camphor and 1 g camphene and pressed in a handpress to a tablet-shaped solid perfumed body. The evaporation rate at room temperature after 15 days amounted to 6 g, with respect to the total weight of the odor improver.

Example 11

15 g hexamethylcyclotrisiloxane, 6 g tricyclodecane, and 1.0 g terpineol oil were homogeneously mixed with each other and then pressed with a hand press to a ball-shaped perfume vehicle. When the sample was left at room temperature, 14 g of the perfumed body had evaporated after 17 days. The same sample, but without the additional perfume terpineol oil, exhibited the same evaporation rate.

Example 12

15 g hexamethylcyclotrisiloxane, 4 g montan wax and 1.0 g of the perfume composition "drom C" were mixed in accordance with Example 4 and then pressed with a handpress to a loosely packed tablet.

The sample was stored at room temperature and then the sublimation rate was determined. A total of 13 g of the perfumed body had evaporated after storage of 17 days.

Example 13

An odor improver tablet consisting of 19 g hexamethylcyclotrisiloxane and 1 g citronella oil in a solution of polyvinyl acetate and polyvinylpyrrolidone was immersed in isopropanol and then dried at room temperature. After drying, a uniform thin coating of polyvinyl acetate/polyvinylpyrrolidone had formed on the surface of the odor improver tablet. The tablet coated with the synthetic coating was stored at room temperature in order to determine the evaporation rate. After 14 days, the odor improver had evaporated with the collapsed synthetic coating remaining behind.

The above test was repeated except that the tablet was immersed two times in the above solution. It was established that the sublimation rate of this tablet was lower than that of the sample that had been immersed only once in the polyvinyl acetate/polyvinylpyrrolidone solution.

Example 14

Two odor improver tablets were prepared, each from 19 g hexamethylcyclotrisiloxane and 1 g isobornyl acetate. The first tablet was then immersed once in a melt of montan wax. After the coating had hardened, the sublimation rate was determined at room temperature. It was 6.8 g after 1 day, calculated with respect to the total weight of the odor improver.

With the second tablet, the immersion into the montan wax melt was carried out three times in order to make a threefold coating on the tablet. The sublimation rate for this sample was only 3.8 g per day.

Example 15

An aerosol was prepared from the following constituents:
40% hexamethylcyclotrisiloxane
4% perfume composition "drom C"
56% fluorocarbon as propellent gas

When the mixture is sprayed from a spray vessel under pressure, a white dry snow forms, which evaporates without residue while perfuming the room, within 2-10 hours in each case according to the amount sprayed.

Claims

1. An odor improver containing a perfumed vehicle material and a perfume, characterized by the fact that it contains hexaalkylcyclotrisiloxane and optionally other evaporable or

nonevaporable added agents to reduce the sublimation rate of the hexaalkylcyclotrisiloxane.

2. An odor improver as in Claim 1, characterized by the fact that it additionally contains cosmetic or disinfectant auxiliary agents or washing aids.

3. An odor improver as in Claim 1, characterized by the fact that the hexaalkylcyclotrisiloxane is a hexa(C_1-C_4-alkyl)cyclotrisiloxane.

4. An odor improver as in Claim 3, characterized by the fact that the hexaalkylcyclotrisiloxane is a hexamethyl-, hexaethyl-, hexapropyl-, hexaisopropyl-, hexabutyl- or hexa-t-butylcyclotrisiloxane.

5. An odor improver as in Claim 1, characterized by the fact that it contains as additives, paraffin, stearin, paraffin oil, esters of resin acids, polyamide resins, ethyl cellulose, vinyl acetate, vinyl chloride copolymers, polyvinyl alcohol, gelatin, starch, epoxy resins, polychloroprene, polyisobutylene, camphor, naphthalene, tetramethylcyclobutanedione, trialkyltrioxane, adhesive substances, camphene, tricyclodecane, montan resin , paraffin wax, montan wax, polyvinyl acetate, polyvinylpyrrolidone, calcium carbonate, clay, aluminum oxide, resinoids, water glass, silicates, silica and/or a propellent gas.

6. An odor improver as in Claim 1, characterized by the fact that it contains as perfume, natural or synthetic perfume oils, hydrocarbons, resinoids, and/or absolutes.

7. An odor improver as in Claim 6, characterized by the fact that it contains as perfume oil, those that contain as functional groups hydroxyl, ether, ester, aldehyde, acid,

nitrile, keto or nitro groups, chlorine atoms, and/or terpene groups.

8. An odor improver as in Claim 1, characterized by the fact that the additives are solid and surround the odor improver in the form of a vapor-permeable coating.

9. An odor improver as in Claim 1, characterized by the fact that it contains 0.5-98% by weight, especially 2-60% by weight, hexaalkylcyclotrisiloxane, with respect to the total weight of the odor improver.

10. An odor improver as in Claim 1, characterized by the fact that it contains 2-50% by weight perfume and/or perfume compositions, with respect to the total weight of the odor improver.

11. An odor improver as in Claim 1, characterized by the fact that it contains 6-50% by weight gaseous, liquid, and/or solid additives, with respect to the total weight of the odor improver.

12. An odor improver as in Claim 1 or 2, characterized by the fact that it contains 3-15% by weight surfactants, washing aids, and/or disinfectants, with respect to the total weight of the odor improver.

13. An odor improver as in Claim 1, which is characterized by the fact that it contains 0.1-1% by weight of at least one alkaline earth metal oxide with respect to the weight of the hexaalkylcyclotrisiloxane.

14. A method for preparation of an odor improver as in one of Claims 1-14, characterized by the fact that the hexaalkylcyclotrisiloxane is mixed with the perfume and/or the perfume composition optionally while adding other auxiliary

agents and the mixture is then molded into an object or the mixture is converted to a sprayable mass.

15. A method as in Claim 14, which is characterized by the fact that the object is immersed into an immersion bath containing at least one of the additives for reduction of sublimation of hexaalkylcyclotrisiloxane or sprayed with a solution or melt containing at least one of the additives, in order to provide the object with a vapor-permeable coating.